FORM PTO-1390 (REV 10-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: FUK-84

U.S. APPLICATION NO. (If known, see 37 CFR 1.5): 09/889269

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/000133	January 13, 2000	January 13, 1999

TITLE OF INVENTION: Metal Material Having Formed Thereon Chromium Oxide Passive Film and Method For Producing the Same, and Parts Contacting with Fluid and System

APPLICANT(S) FOR DO/EO/US: Tadahiro OHMI et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. [ ] This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. [X] The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [ ] is attached hereto (required only if not communicated by the International Bureau).
   b. [X] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. [X] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [X] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 16 below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [X] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [ ] Other items or information:

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/889269	PCT/JP00/000133	FUK-84

17. ☒ The following fees are submitted:	CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
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Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ --00--	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	4 - 20 =	0	X **$18.00**	$ --00--	
Independent claims	2 - 3 =	0	X **$80.00**	$ --00--	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$270.00**	$ --00--	
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				$ --00--	
SUBTOTAL =				$ 860.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐20 ☐30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ --00--	
TOTAL NATIONAL FEE =				$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ --00--	
TOTAL FEES ENCLOSED =				$ 860.00	
				Amount to be refunded:	$
				charged:	$

a. ☒ A check in the amount of $ 860.00 to cover the above fees is enclosed. Check No. 5343

b. ☐ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 501157. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

CUSTOMER NO. 22855

22855

Telephone: 219-485-6001
Facsimile: 219-486-2794

SIGNATURE

Randall J. Knuth

NAME

34,644

REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	)
Tadahiro OHMI et al.	) Group:
Serial No.:	)
Filed: July 13, 2001	) Examiner:
Title: METAL MATERIAL HAVING FORMED THEREON CHROMIUM OXIDE PASSIVE FILM AND METHOD FOR PRODUCING THE SAME, AND PARTS CONTACTING WITH FLUID AND SYSTEM FOR SUPPLYING FLUID AND EXHAUSTING GAS	)

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Applicant hereby submits the following Amendment.

IN THE CLAIMS

1. (Amended) Metallic material provided with a chromium-oxide passivation film compromising a passivation film consisting of chromium oxide obtained by oxidizing a chromium coat on the metallic material of which surface roughness (Ra) is not more than [1.5im] 1.5μm.

2. (Amended) The metallic material provided with the chromium-oxide passivation film according to claim 1, said film having pin holes wherein pin holes of said chromium-oxide passivation film are filled.

3. (Amended) A method for manufacturing metallic material on which a chromium-oxide passivation film is formed, comprising the step of:

forming the passivation film consisting of chromium oxide by applying heat treatment in an oxidizing atmosphere after coating chromium on the metallic material of [which] the surface roughness (Ra) of [a coat] metallic material surface is not more than [1.5im] 1.5μm.

4. (Amended) [Parts contracting with fluid and a] A fluid supplying/exhaust system for manufacturing semiconductors, comprising metallic material having a chromium-oxide passivation film according to claim 1.

IN THE ABSTRACT

Please delete the abstract on file and replace it with the attached ABSTRACT OF THE DISCLOSURE.

If the Examiner has any questions or comments that would speed prosecution of this case, he is invited to call the undersigned at 219/485-6001.

Respectfully submitted,

Randall J. Knuth
Registration No. 34,644

RJK/jrw
Encs: Clean Claims
Replacement
ABSTRACT OF THE DISCLOSURE
Return Postcard

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CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Hon. Commissioner of Patents and Trademarks, Washington, D.C. 20231, on: July 13, 2001 .

Randall J. Knuth, Regis. No. 34,644
Name of Registered Representative

Signature

July 13, 2001
Date

CLEAN CLAIMS

1. Metallic material provided with a chromium-oxide passivation film compromising a passivation film consisting of chromium oxide obtained by oxidizing a chromium coat on the metallic material of which surface roughness (Ra) is not more than 1.5μm.

2. The metallic material provided with the chromium-oxide passivation film according to claim 1, said film having pin holes wherein pin holes of said chromium-oxide passivation film are filled.

3. A method for manufacturing metallic material on which a chromium-oxide passivation film is formed, comprising the step of:

forming the passivation film consisting of chromium oxide by applying heat treatment in an oxidizing atmosphere after coating chromium on the metallic material of the surface roughness (Ra) of metallic material surface is not more than 1.5μm.

4. A fluid supplying/exhaust system for manufacturing semiconductors, comprising metallic material having a chromium-oxide passivation film according to claim 1.

ABSTRACT OF THE DISCLOSURE

The object of the present invention is to form a chromium-oxide film, excellent in corrosion resistance, without containing an oxide film of other metal onto the metallic material. The chromium-oxide passivation film, excellent in corrosion resistance, without containing the oxide film of other metal can be formed inexpensively and in a short time, and a fluid supplying system for safely supplying fluid with hard corrosivity is able to be provided. One step of forming the passivation film consisting of a chromium oxide layer by giving heat treatment, in an oxidizing atmosphere, after coating chromium on the metallic material having a surface roughness (Ra) not more than 1.5μm.

Substitute Specification

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METAL MATERIAL HAVING FORMED THEREON CHROMIUM OXIDE PASSIVE FILM AND METHOD FOR PRODUCING THE SAME, AND PARTS CONTACTING WITH FLUID AND SYSTEM FOR SUPPLYING FLUID AND EXHAUSTING GAS

BACKGROUND OF THE INVENTION

1. Field of the invention.

The present invention relates to metallic material on which a chromium-oxide passivation film is formed and a method for manufacturing the same, and a fluid supplying/exhaust system.

2. Description of the related art.

In semiconductor manufacturing technology, gases with a hard corrosive action such as hydrogen chloride or hydrogen bromide or gases with a hard decomposing action such as silane, diborane, phosphine or the like have been used. Since gases hard in corrosivity easily corrode conventional stainless steel (SUS 316L) to result in metal contamination due to corrosion on semiconductor substrates, a semiconductor with high reliability has been difficult to manufacture.

Moreover, since the gases with the hard decomposing action are decomposed easily due to nickel in catalytic action on the stainless steel, the desired gases are difficult to supply with a desired concentration, semiconductors high in reliability have been difficult to manufacture. In recent years, a technology for

forming a chromium-oxide passivation film has been introduced in order to solve the problems described above.

However, development of the metallic material, and surface treatment technology prior to oxidizing treatment or various technologies such as a technology supplying an oxidizing atmosphere such as temperature and a component ratio in oxidizing gases have been required in order to form the chromium-oxide passivation film. Therefore, it has been impossible to inexpensively form the chromium-oxide passivation film onto the optional metallic material and parts.

Moreover, although it has been a prior art technology, coating chromium for improvement of corrosion resistance, it has not been excellent since it is poor in adhesion, moreover, chromium has large internal stress, which causes cracks, so that corrosion is caused at an interface between metallic material and the coat film. Although a crack-free chromium coating technology has been developed in order to solve these cracks, fracture due to distortion during processing may occur since the film thickness is uneven, thereby causing corrosion.

Moreover, there has been problem that although a dual-layer chromium coating technology has been developed in order to solve this fracturing due to distortion, this technology uses different coating processes which results in an increase in cost, so that it is poor in productivity.

Moreover, there has been a technology that heat treatment is performed after metal coating. However, there have been problems

in these technologies that vacancies (pin holes) exist on the surface after coating, the coat film may peel off, or the film obtained after heat treatment is a composite-oxide film or may have a property of ceramic, and since the metal material or the substrate layer is contact with corrosive gases when such vacancies exist, corrosion progresses on the interface between the metal of the substance layer and the coat film, and the desired corrosion resistance can not be obtained because of the composite-oxide film. Furthermore, it is poor in workability because it has the property of ceramic.

The object of the invention is to provide a metallic material on which a chromium-oxide passivation film (high in productivity) is formed and a method for manufacturing the same by forming this chromium-oxide passivation film, having excellent corrosion resistance, inexpensively and quickly.

The object of the invention is to provide parts contacting with fluid and a fluid supplying system capable of safely supplying safely fluid hard in corrosivity by forming the chromium-oxide film excellent in corrosion resistance without containing an oxide film of other metal.

SUMMARY OF THE INVENTION

The metallic material according to the invention on which chromium-oxide passivation is formed comprises the passivation film consisting of the chromium oxide obtained by oxidizing the chromium coat on the metallic material of which the surface roughness (Ra) is not more than 1.5μm.

A method for manufacturing the metallic material according to the invention on which the chromium-oxide passivation is formed comprises a step of forming the passivation film consisting of the chromium oxide by applying heat treatment in an oxidizing atmosphere after coating chromium on the metallic material of which the surface roughness (Ra) of a coated surface is not more than 1.5μm.

Parts contacting with fluid and a fluid supplying/exhaust system according tot he invention are characterized by that these are constituted by the metallic material on which the chromium-oxide passivation film having the passivation film consisting of the chromium oxide obtained by oxidizing the chromium coat are formed on the metallic material of which surface roughness (Ra) is not more than 1.5μm.

BRIEF DESCRIPTION OF THE DRAWINGS

The above-mentioned and other features and advantages of this invention, and the manner of attaining them, will become more apparent and the invention will be better understood by reference to the following description of an embodiment of the invention taken in conjunction with the accompanying drawings, wherein:

Fig. 1 is a schematic view of a gas supplying system used in a chromium-oxide passivation film according to the invention;

Fig. 2 is a view showing a result of evaluating chromium-oxide passivation film after oxidizing treatment by photoelectron spectroscopy;

Fig. 3 is a view showing results of evaluation surface roughness (Ra) dependence of corrosion resistance of the chromium-oxide passivation film according to the invention by SEM observation; and

Fig. 4 is a view showing results by SEM observation of the sample after a corrosion test by chlorine gas of the sample by using a method for manufacturing the chromium-oxide passivation film according to the invention and a sample which oxidizing treatment is not given, and sample after cleaning with ultra pure water after the corrosion test.

Corresponding reference characters indicate corresponding parts throughout the several views. The exemplification set out herein illustrates one preferred embodiment of the invention, in one form, and such exemplification is not to be construed as limiting the scope of the invention in any manner.

DETAILED DESCRIPTION OF THE INVENTION

Explanations of Characters

101 flow-rate adjustment device

102 fluid control valve

103 reaction chamber

Best Mode for Carrying out the Invention

This invention comprises a step of forming a passivation film consisting of chromium oxide excellent in corrosion resistance on an optional metallic material by giving heat treatment in an oxidizing atmosphere on a surface obtained by

coating chromium onto the metallic material (for example, copper material) of which surface roughness (Ra) is not more than 1.5μm.

In the invention, a contact ability of an interface between the metallic material and a coat film is improved by coating chromium onto the metallic material of which the surface roughness (Ra) is not more than 1.5μm, in addition to strengthen a coupling force of the interface by applying heat treatment solves the poorness of the conventional adhesion, and in addition, the chromium-oxide passivation film excellent in corrosion resistance can be formed by applying oxidizing treatment.

This invention comprises the step of forming the passivation film consisting of the sealed chromium oxide, excellent in corrosion resistance, by applying heat treatment in the oxidizing gas atmosphere on the surface of the metallic material on which chromium is coated. According to the invention, the problem of interface corrosion caused due to the presence of vacancies (pin holes) can be solved, in addition, the chromium-oxide passivation film, excellent in corrosion resistance, can be formed by applying oxidizing treatment.

In this invention, definition of the metallic material, definition of the shape of the parts and precise control of the oxidizing atmosphere are not required, and it becomes possible to form the chromium-oxide passivation film onto the optional metallic material and the parts inexpensively as compared to a chromium-oxide passivation treatment of the prior art. A

Definition of the metallic material and the shape of the parts and precise control of the oxidizing atmosphere are not required, whereby improvement in productivity can be realized.

Although there have been problems in the conventional chromium-oxide passivation treatment technology that there is a problem in production cost and productivity is poor, since the concentration of the oxidizing gas is low as 10 ppm to several hundreds ppm, moreover, the range of the concentration also is narrow and so use of the special parts for an oxidizing-gas supplying system and a special diluting technology are required in order to control the concentration precisely and monitor for control of the concentration also is required in treatment temperature. The range of the forming condition for formation of the chromium-oxide passivation film can be set widely according to the present invention, whereby a chromium-oxide passivation treatment inexpensive and high in productivity can be realized.

The chromium-oxide passivation film, excellent in corrosion resistance, becomes possible to be formed on the optional metallic material and the parts inexpensively and in a short time according to the invention, the fluid supplying system capable of supplying fluid with the hard corrosive action can safely be constructed.

Embodiments

Although a forming technology of a chromium-oxide passivation film as well as the parts contacting with fluid a fluid supplying/exhaust system according to the invention will be

described with reference to the drawings as described below, the invention should not be limited to these embodiments.

Although a chromium-coat film used for this experiment is deposited by a planting method, in addition thereto, deposition may be performed by coating technologies such as an ion-plating method, HIP method, a sputtering method. Deposition may be performed by a two-step forming method which is designed to be formed by the sputtering method initially and then to be formed by the plating method thereon.

Moreover, baking is preferably performed once at a low temperature of 100°C to 200°C in a high-purity inert gas atmosphere (the concentration of moisture is not more than 10 ppm) and then heat treatment is performed, when forming the chromium-coat film by a wet-type plating method.

Moreover, an annealing processing is preferably performed after heat treatment.

Moreover, austenite system stainless steel (SUS316L) was used for the metallic material to be oxidized.

Embodiment 1

Fig. 1 is a schematic view of a gas supplying system performing treatment for the chromium-oxide passivation film according to the invention. Argon is introduced as an inert gas and oxygen as an oxidizing gas for dilution in the gas supplying system. The chromium-oxide passivation film was formed using this gas supplying system.

In the embodiment, an influence of the surface roughness (Ra) of the metallic material to be oxidized was searched by corrosion test with chlorine gas. Oxidizing conditions are 500°C, 30 min, oxygen of 50% (diluted by argon).

Fig. 2 shows a result measured by evaluating chromium-oxide passivation film by a ESCA-100, made by Shimazu Seisakusyo, after oxidizing treatment.

From the results, it was verified that the chromium-oxide passivation film of substantially 100% has been formed, which is approximately 30 nm from the outermost surface.

The corrosion test is performed under the condition of sealing chlorine gas of 100% under not more than 5 Kgf/cm^2 at 100°C for 24Hr through an accelerated test. Surface observation was performed by a scanning electron microscope JSM-6401F, made by Nippon Densi Kabusikikaisya, after oxidizing treatment.

Fig. 3 shows results after the corrosion test. From the results, it was not verified that corrosive products exist in the case of the surface roughness (Ra) of not more than 1.5μm, whereas the corrosive products have been scattered in the case of not less than 2μm. It is speculated that adhesion of the interface between the metallic material and the chromium-coat film deteriorates, so that clearance corrosion is caused as the surface roughness (Ra) becomes large.

From the results as described above, it is speculated that the chromium-oxide passivation film having corrosion resistance, which is excellent in adhesion of the interface between the

metallic material and the chromium-coat film can be formed when the surface roughness (Ra) of not more than 1.5μm.

Moreover, the chromium-oxide passivation film further excellent in durability can be formed by allowing to coat a metal on the metallic material to be oxidized in pretreatment for forming the chromium-coat film to improve adhesion onto chromium and to prevent crack and fracture due to distortion.

Moreover, the more close-grained and tight chromium-oxide passivation film can be formed by doping with hydrogen into the oxidizing gas.

Embodiment 2

The accelerated corrosion test of the sample on which oxidizing treatment was given in the same condition as Embodiment 1 and the sample on which oxidizing treatment was not given was performed under the condition of sealing chlorine gas of 100% under not more than 5 Kgf/cm^2 at 100°C for 24Hr.

Fig. 4 shows the results by SEM observation after the corrosion test by JSM-6301F, made by Nippon Densi Kabusikikaisya after oxidizing treatment, as well as the results by SEM observation of the sample after cleaning with ultra pure water after corrosion test.

From the results, it was not verified that corrosion exist for the sample on which oxidizing treatment was given, whereas the corrosive products have been scattered for the sample on which oxidizing treatment was not given.

Moreover, it has been speculated from the results that SEM observation was performed after cleaning the sample after corrosion test with ultra pure water to remove the corrosive products or the like that changes was not observed for the sample on which oxidizing treatment was given, whereas there were the vacancies (the pin holes) of a diameter of approximately 0.1μm on the site where the corrosive products were removed for the sample on which oxidizing treatment was not given, and this was corrosion contributed to the pin holes existing after plating.

It has been found by these experiments that there are the vacancies on the coat film used for the prior art, and the corrosion caused by the vacancies is progressing, however, the vacancies are filled according to the invention, whereby the chromium-oxide passivation film which is close-grained and excellent in corrosion resistance can be formed on the outermost surface.

Applicability for the Industry

According to the present invention, a passivation film consisting of chromium oxide, excellent in corrosion resistance, form onto metallic material.

According to the present invention, the conventional problem of interface corrosion caused due to the presence of the crack, fracture due to distortion and the vacancies (pin holes) or the like can be solved, in addition, the chromium-oxide passivation film excellent in corrosion resistance can be formed by applying oxidizing treatment.

According to the present invention, definition of the metallic material, definition of the shape of the parts and precise control of the oxidizing atmosphere are not required, and it becomes possible to form the chromium-oxide passivation film onto the optional metallic material and parts inexpensively as compared to a chromium-oxide passivation treatment of the prior art, and definition of the metallic material and the shape of the parts and precise control of the oxidizing atmosphere are not required, whereby improvement in productivity is realized.

According to the invention, the fluid supplying system capable of supplying fluid with hard corrosive action in safety can be constructed.

While this invention has been described as having a preferred design, the present invention can be further modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the invention using its general principles. Further, this application is intended to cover such departures from the present disclosure as come within known or customary practice in the art to which this invention pertains and which fall within the limits of the appended claims.

Specification

Metal material having formed thereon chromium oxide passive film and method for producing the same, and parts contacting with fluid and system for supplying fluid and exhausting gas

Technical Field of the Invention

The present invention relates to metallic material on which a chromium-oxide passivation film is formed and a method for manufacturing the same, and a fluid supplying / exhaust system.

Background Art

In semiconductor manufacturing technology, gases with a hard corrosive action such as hydrogen chloride or hydrogen bromide or gases with a hard decomposing action such as silane, diborane, phosphine or the like have been used. Since the gases hard in corrosivity easily corrode usually used stainless steel (SUS 316L) to result in metal contamination due to corrosion on a semiconductor substrate, a semiconductor with high reliability has been difficult to manufacture.

Moreover, since the gases with the hard decomposing action are decomposed easily due to nickel hard in catalytic action on the stainless steel, and desired gases are difficult to supply with a desired concentration, the semiconductor high in reliability has been difficult to manufacture. In recent years, a technology for forming a chromium-oxide passivation film has been introduced in order to solve the problems described above.

However, a development of the metallic material, and a surface treatment technology prior to oxidizing treatment or various technologies such as a technology for supplying an oxidizing atmosphere such as temperature and a component ratio in oxidizing gases have been required in order to form the chromium-oxide passivation film. Therefore, it has been impossible to form the chromium-oxide passivation film onto the optional metallic material and parts inexpensively.

Moreover, although it has been a technology coating chromium for improvement of corrosion resistance according to the prior art, it has been not excellent since it is poor in adhesion, moreover, chromium has a large internal stress, crack is caused, so that corrosion is caused at an interface between the metallic material and the coat film. Although a crack-free chromium coating technology has been developed in order to solve these crack, fracture due to distortion at processing are caused since a film thickness is thicken excessively, thereby corrosion being caused.

Moreover, there has been problem that although a dual-layers chromium coating technology has been developed in order to solve this fracture due to distortion, this technology also is different each other in coating processes and results in an increase in cost, so that it is poor in productivity.

Moreover, there has been a technology that heat treatment is performed after metal coating. However, there have been problems in these technologies that vacancies (pin holes) exist on the surface after coating, the coat film is peeled off, or

the film obtained after heat treatment is a composite-oxide film or has a property of ceramic, and since the metal material of the substrate layer is contact with corrosive gases when vacancies exist, corrosion progresses on the interface between the metal of the substrate layer and the coat film, and the desired corrosion resistance can not be obtained because of the composite-oxide film, furthermore, it is poor in workability because of the property of ceramic.

The object of the invention is to provide metallic material on which the chromium-oxide passivation film high in productivity is formed and a method for manufacturing the same by forming the chromium-oxide passivation film excellent in corrosion resistance inexpensively and in a short time.

The object of the invention is to provide the parts contacting with fluid and a fluid supplying system capable of supplying safely fluid hard in corrosivity by forming the chromium-oxide film excellent in corrosion resistance without containing an oxide film of other metal.

Disclosure of the Invention

The metallic material according to the invention on which the chromium-oxide passivation is formed comprises the passivation film consisting of the chromium oxide obtained by oxidizing the chromium coat on the metallic material of which surface roughness (Ra) is not more than 1.5im.

A method for manufacturing the metallic material according to the invention on which the chromium-oxide passivation is

formed comprises a step of forming the passivation film consisting of the chromium oxide by applying heat treatment in an oxidizing atmosphere after coating chromium on the metallic material of which surface roughness (Ra) of a coat surface is not more than 1.5im.

Parts contacting with fluid and a fluid supplying / exhaust system according to the invention are characterized by that these are constituted by the metallic material on which the chromium-oxide passivation film having the passivation film consisting of the chromium oxide obtained by oxidizing the chromium coat are formed on the metallic material of which surface roughness (Ra) is not more than 1.5im.

Brief Description of the Drawings

Fig. 1 is a schematic view of a gas supplying system used in a chromium-oxide passivation film according to the invention.

Fig. 2 is a view showing a result by evaluating chromium-oxide passivation film after oxidizing treatment by photoelectron spectroscopy.

Fig. 3 is a view showing results by evaluating surface roughness (Ra) dependence of corrosion resistance of the chromium-oxide passivation film according to the invention by SEM observation.

Fig. 4 is a view showing results by SEM observation of the sample after corrosion test by chlorine gas of sample by using a method for manufacturing the chromium-oxide passivation film according to the invention and sample which oxidizing treatment

is not given, and sample after cleaning with ultra pure water after corrosion test.

(Explanations of Characters)

101 flow-rate adjustment device

102 fluid control valve

103 reaction chamber

Best Mode for Carrying out the Invention

This invention comprises a step of forming a passivation film consisting of chromium oxide excellent in corrosion resistance on an optional metallic material by giving heat treatment in an oxidizing atmosphere on a surface obtained by coating chromium onto the metallic material (for example, copper material) of which surface roughness (Ra) is not more than 1.5im.

In the invention, a contact ability of an interface between the metallic material and a coat film is improved by coating chromium onto the metallic material of which surface roughness (Ra) is not more than 1.5i, in addition, to strengthen a coupling force of the interface by applying heat treatment to solve the poorness of the conventional adhesion, and in addition, the chromium-oxide passivation film excellent in corrosion resistance can be formed by applying oxidizing treatment.

This invention comprises a step of forming the passivation film consisting of the sealed chromium oxide excellent in corrosion resistance by applying heat treatment in the oxidizing gas atmosphere on the surface of the metallic material

on which chromium is coated. According to the invention, the problem of interface corrosion caused due to the presence of vacancies (pin holes) can be solved, in addition, the chromium-oxide passivation film excellent in corrosion resistance can be formed by applying oxidizing treatment.

In this invention, definition of the metallic material, definition of the shape of the parts and precise control of the oxidizing atmosphere are not required, and it becomes possible to form the chromium-oxide passivation film onto the optional metallic material and the parts inexpensively as compared to a chromium-oxide passivation treatment of the prior art. Definition of the metallic material and the shape of the parts and precise control of the oxidizing atmosphere are not required, whereby improvement in productivity can be realized.

Although there have been problems in the conventional chromium-oxide passivation treatment technology that there is a problem in production cost and productivity is poor, since the concentration of the oxidizing gas is low as is 10 ppm to several hundreds ppm, moreover, the range of the concentration also is narrow and so use of special parts for an oxidizing-gas supplying system and a special diluting technology are required in order to control the concentration precisely and monitor for control of the concentration also is required in treatment temperature, the range of the forming condition for formation of the chromium-oxide passivation film can be set widely according to the present invention, whereby the chromium-oxide passivation treatment inexpensive and high in productivity can

be realized.

The chromium-oxide passivation film excellent in corrosion resistance becomes possible to form on the optional metallic material and the parts inexpensively and in a short time according to the invention, the fluid supplying system capable of supplying fluid with the hard corrosive action in safety can be constructed.

Embodiments

Although a forming technology of a chromium-oxide passivation film as well as the parts contacting with fluid and a fluid supplying / exhaust system according to the invention will be described with reference to the drawings as described below, the invention should not be limited to these embodiments.

Although a chromium-coat film used for this experiment is deposited by a plating method, in addition thereto, deposition may be performed by coating technologies such as an ion-plating method, HIP method, a sputtering method. Deposition may be performed by two-steps forming method which is designed to form by the sputtering method initially and then to form by the plating method thereon.

Moreover, baking is preferably performed once at low temperature of 100 ºC to 200 ºC in high-purity inert gas atmosphere (the concentration of moisture is not more than 10 ppm) and then heat treatment is performed, when forming the chromium-coat film by a wet-type plating method.

Moreover, an annealing processing is preferably performed

after heat treatment.

Moreover, austenite system stainless steel (SUS316L) was used for the metallic material to be oxidized.

(Embodiment 1)

Fig. 1 is a schematic view of a gas supplying system performing treatment for the chromium-oxide passivation film according to the invention. Argon is introduced as an inert gas and oxygen as an oxidizing gas for dilution in the gas supplying system. The chromium-oxide passivation film was formed using this gas supplying system.

In this embodiment, an influence of the surface roughness (Ra) of the metallic material to be oxidized was searched by corrosion test with chlorine gas. Oxidizing conditions are 500 ºC, 30 min, oxygen of 50 % (diluted by argon).

Fig. 2 shows a result measured by evaluating chromium-oxide passivation film by ESCA100, made by Shimazu Seisakusyo after oxidizing treatment.

From the results, it was verified that the chromium-oxide passivation film of substantially 100 % has been formed, which is approximately 30 nm from the outermost surface.

The corrosion test is performed under the condition of sealing chlorine gas of 100 % under not more than 5 Kgf/cm^2 at 100 ºC for 24Hr through an accelerated test. Surface observation was performed by JSM-6401F, made by Nippon Densi Kabusikikaisya after oxidizing treatment.

Fig. 3 shows results after the corrosion test. From the results, it was not verified that corrosive products exist in

the case of the surface roughness (Ra) of not more than 1.5㎛, whereas the corrosive products have been scattered in the case of not less than 2㎛. It is guessed that adhesion of the interface between the metallic material and the chromium-coat film deteriorates, so that clearance corrosion is caused as the surface roughness (Ra) becomes large.

From the results as described above, it is guessed that the chromium-oxide passivation film having corrosion resistance, which is excellent in adhesion of the interface between the metallic material and the chromium-coat film can be formed when the surface roughness (Ra) of not more than 1.5㎛.

Moreover, the chromium-oxide passivation film further excellent in durability can be formed by allowing to coat a metal on the metallic material to be oxidized in pretreatment for forming the chromium-coat film to improve adhesion onto chromium and to prevent crack and fracture due to distortion.

Moreover, the more close-grained and tight chromium-oxide passivation film can be formed by doping with hydrogen into the oxidizing gas.

(Embodiment 2)

The accelerated corrosion test of the sample on which oxidizing treatment was given in the same condition as Embodiment 1 and the sample on which oxidizing treatment was not given was performed under the condition of sealing chlorine gas of 100 % under not more than 5 Kgf/cm^2 at 100 ºC for 24Hr.

Fig. 4 shows the results by SEM observation after the corrosion test by JSM-6401F, made by Nippon Densi Kabusikikaisya after

oxidizing treatment, as well as the results by SEM observation of the sample after cleaning with ultra pure water after corrosion test.

From the results, it was not verified that corrosion exist for the sample on which oxidizing treatment was given, whereas the corrosive products have been scattered for the sample on which oxidizing treatment was not given.

Moreover, it has been guessed from the results that SEM observation was performed after cleaning the sample after corrosion test with ultra pure water to remove the corrosive products or the like that changes was not observed for the sample on which oxidizing treatment was given, whereas there were the vacancies (the pin holes) of a diameter of approximately 0.1㎛ on the site where the corrosive products were removed for the sample on which oxidizing treatment was not given, and this was corrosion contributed to the pin holes existing after plating.

It has been found by these experiments that there are the vacancies on the coat film used for the prior art, and corrosion caused by the vacancies is progressing, however, the vacancies are filled according to the invention, whereby the chromium-oxide passivation film which is close-grained and excellent in corrosion resistance can be formed on the outermost surface.

Applicability for the Industry

According to the present invention, the passivation film consisting of chromium oxide excellent in corrosion resistance

onto the optional metallic material can be formed.

According to the present invention, the conventional problem of interface corrosion caused due to the presence of the crack, fracture due to distortion and the vacancies (pin holes) or the like can be solved, in addition, the chromium-oxide passivation film excellent in corrosion resistance can be formed by applying oxidizing treatment.

According to the present invention, definition of the metallic material, definition of the shape of the parts and precise control of the oxidizing atmosphere are not required, and it becomes possible to form the chromium-oxide passivation film onto the optional metallic material and parts inexpensively as compared to a chromium-oxide passivation treatment of the prior art, and definition of the metallic material and the shape of the parts and precise control of the oxidizing atmosphere are not required, whereby improvement in productivity is realized.

According to the invention, the fluid supplying system capable of supplying fluid with the hard corrosive action in safety can be constructed.

What is claimed is:

1. Metallic material provided with a chromium-oxide passivation film comprising a passivation film consisting of chromium oxide obtained by oxidizing a chromium coat on the metallic material of which surface roughness (Ra) is not more than 1.5im.

2. The metallic material provided with the chromium-oxide passivation film according to claim 1, wherein pin holes of said chromium-oxide passivation film are filled.

3. A method for manufacturing metallic material on which a chromium-oxide passivation film is formed, comprising the step of :

forming the passivation film consisting of chromium oxide by applying heat treatment in an oxidizing atmosphere after coating chromium on metallic material of which surface roughness (Ra) of a coat surface is not more than 1.5im.

4. Parts contacting with fluid and a fluid supplying / exhaust system, comprising metallic material having a chromium-oxide passivation film according to claim 1.

FIG. 1

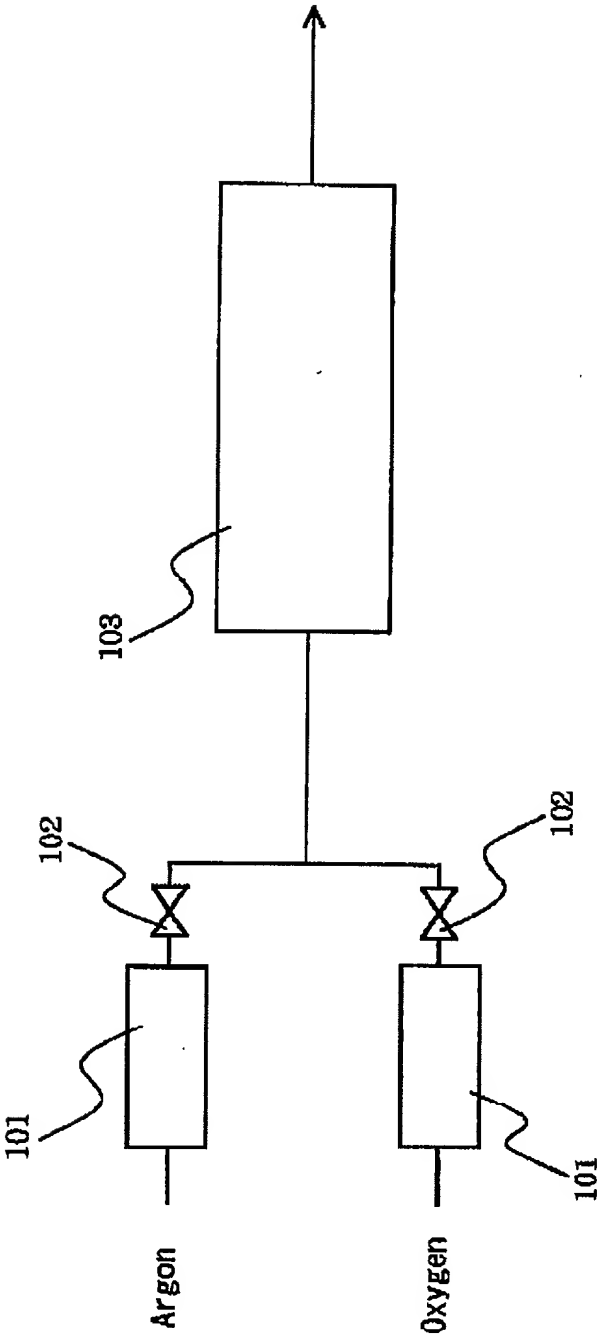


FIG. 2

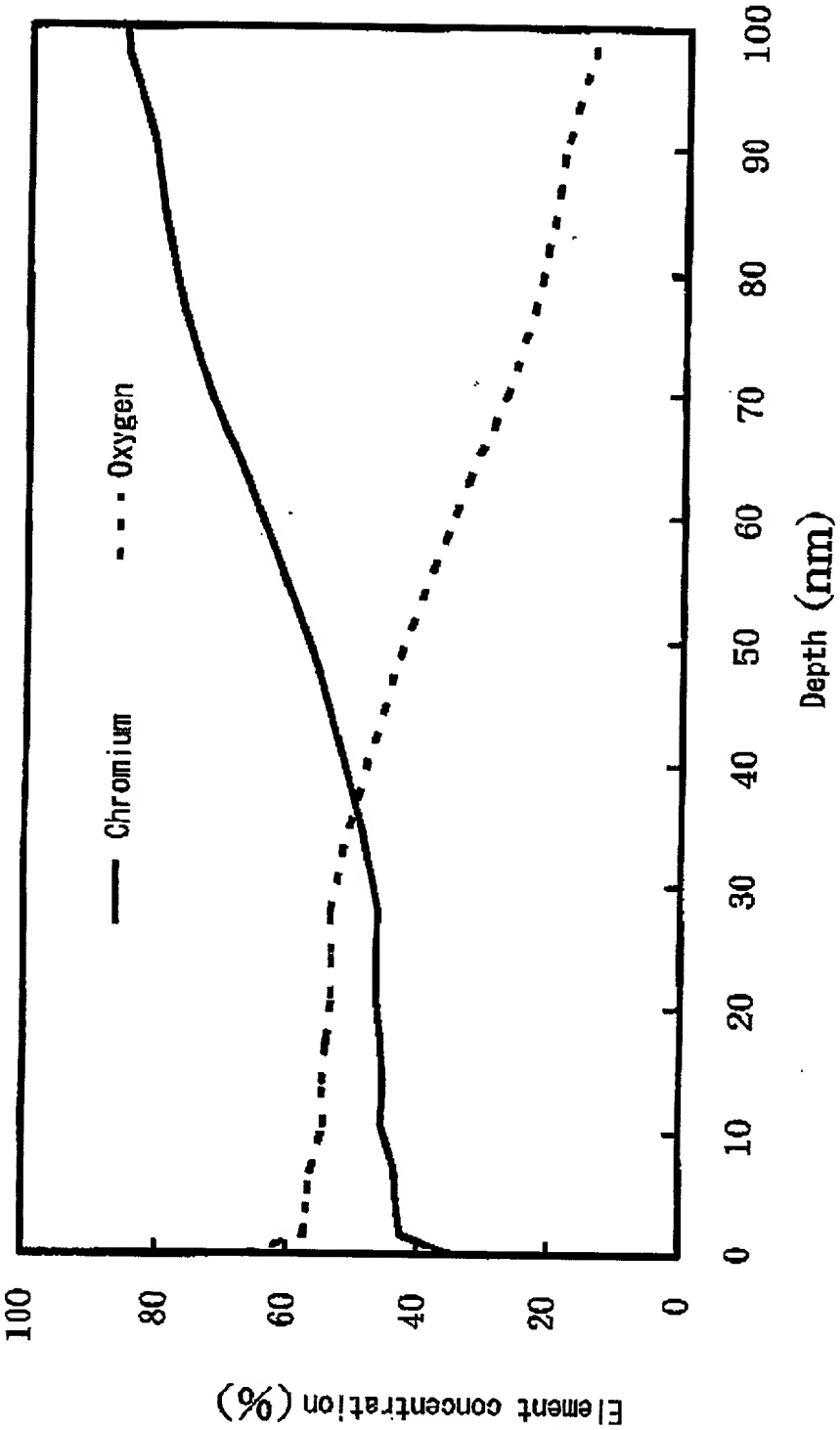

Chromium
Oxygen
Depth (nm)
Element concentration (%)
0
10
20
30
40
50
60
70
80
90
100
100
80
60
40
20
0

FIG. 3

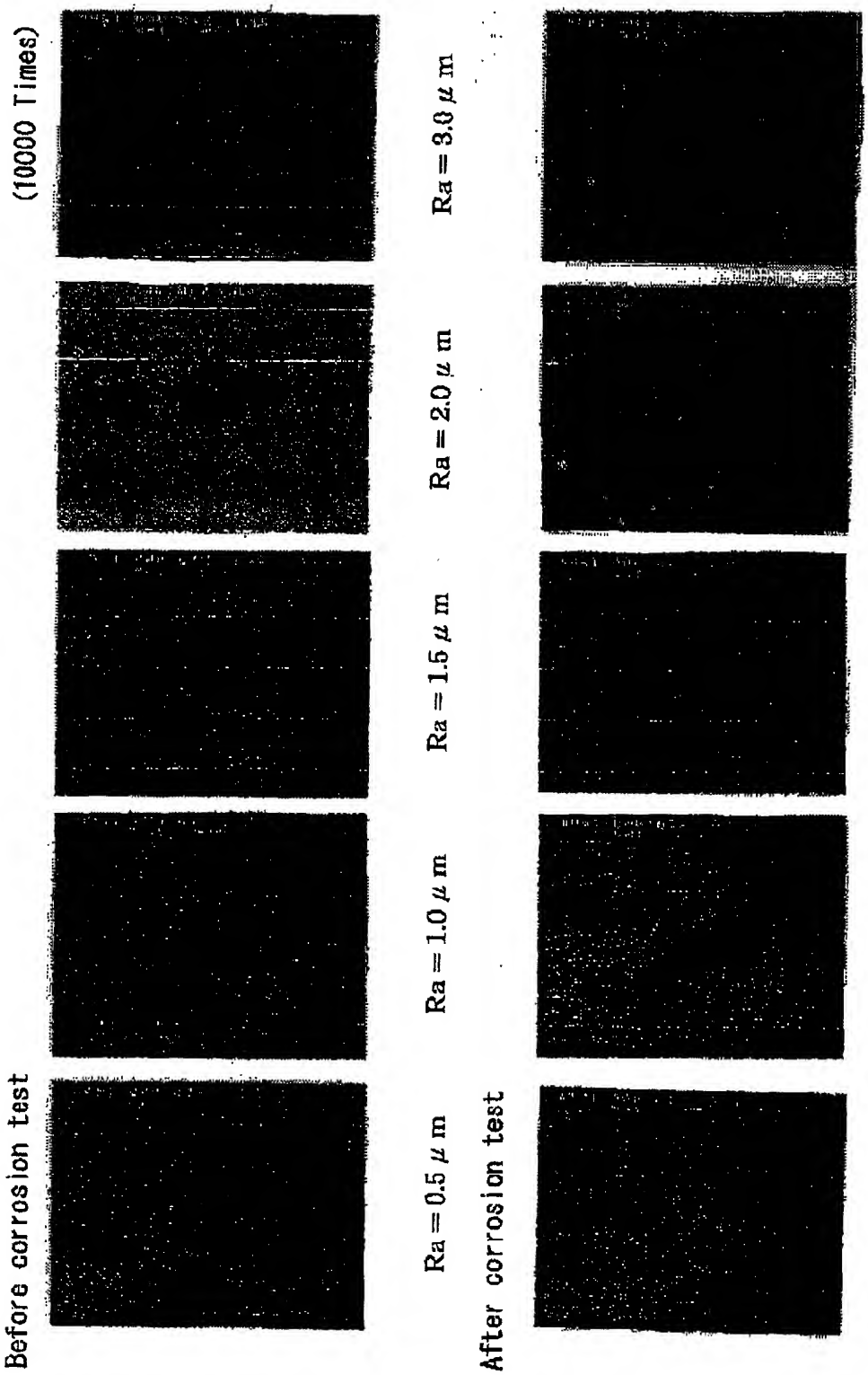
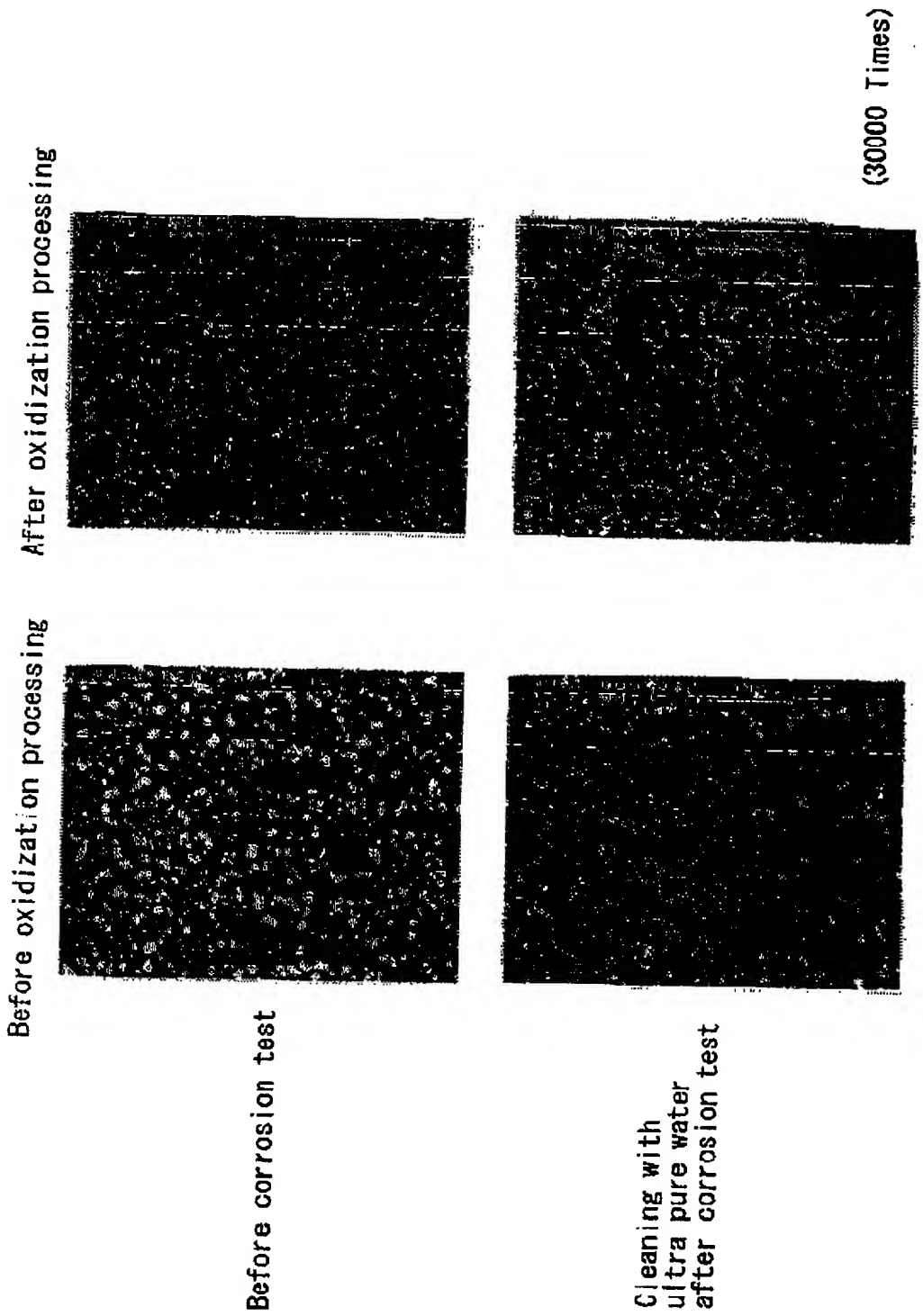

(10000 Times)
Ra = 3.0 μm
Ra = 2.0 μm
Ra = 1.5 μm
Ra = 1.0 μm
Ra = 0.5 μm
Before corrosion test
After corrosion test

FIG. 4


(30000 Times)
After oxidization processing
Before oxidization processing
Before corrosion test
Cleaning with ultra pure water after corrosion test

US #4

ATTORNEY'S DOCKET NO. FUK-84

PCT/USA NATIONAL DECLARATION AND POWER OF ATTORNEY
FOR U.S. PATENT APPLICATIONS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
UNDER 35 U.S.C. SECTION 371(c)(4)

As a below named inventor, we hereby declare that:

Our residence, post office address and citizenship are as stated below next to my name:

I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named below) of the invention described and claimed in international application No. PCT/JP00/000133 entitled: METAL MATERIAL HAVING FORMED THEREON CHROMIUM OXIDE PASSIVE FILM AND METHOD FOR PRODUCING THE SAME, AND PARTS CONTACTING WITH FLUID AND SYSTEM FOR SUPPLYING FLUID AND EXHAUSTING GAS and as amended on _____ (if any), which I have reviewed, and I understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above and for which I solicit a patent; that I do not know and do not believe that this invention was ever known or used in the United States of America before my or our invention or discovery thereof, or patented or described in any printed publication in any country before my or our invention or discovery thereof, or more than one year prior to my international application; that this invention was not in public use or on sale in the United States of America for more than one year prior to my international application; that this invention has not been patented or made the subject of an inventor's certificate issued before the date of my international application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months before my international application; that I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application; and that prior to filing said international application, applications for patent or inventor's certificate on this invention of discovery which have been filed by me or my legal representatives or assigns in any country foreign to the United States of America are as follows:

(a) none filed more than 12 months prior to said international application, unless named below:

(b) earliest filed less than 12 months prior to said international application (the priority of which is hereby claimed under 35 U.S.C. Section 365):

JP 11/7092 filed January 13, 1999

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a), which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

(Application Serial No.)	(Filing Date)	(Status)(patented, pending, abandoned)

I hereby appoint Randall J. Knuth, Regis. No. 34,644, Victor F. Lohmann, III, Regis. No. 33,951 and Vincent P. Merz, Jr., Regis. No. 45,722 of the firm of RANDALL J. KNUTH, P.C., as attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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